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Interface modification for increased fracture toughness in reaction-formed yttrium aluminum garnet/alumina eutectic composites

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The validity of controlling interfacial toughness in reaction-formed composites was explored using solid-state reaction processing and microanalysis techniques. A variety of rare-earth oxides was added to a yttrium aluminum garnet (YAG)/alumina powder mixture and then melted in air. Some melts retained the crystallography and microstructure of the pure, binary YAG–alumina eutectic. Using scanning transmission electron microscopy in conjunction with energy dispersive X-ray spectroscopy, rare-earth ions were observed both to segregate to the YAG/alumina interface and to form a third phase. Some evidence of increased crack deflection at these interfaces was observed via indentation fracture.

I. INTRODUCTION

The production of tough, reliable ceramic composites is a primary thrust of structural ceramics research. In brittle–brittle composites, a common approach for increasing fracture toughness has been to weaken the interface between fiber and matrix or between layers by coating the fiber with weakly bonding oxide species,[1,2,3] refractory metals,[4] easy-cleaving oxides,[5,6] or porous structures.[1,7] In each case, the strategy is to promote crack deflection and interface delamination at the fiber–matrix interface or at the coating–fiber interface. This *ex situ* toughened approach has had some success, especially in the case of monazite-coated fibers[1] and other ABO_4[3] coatings on fibers. However, for both the weakly bonding coatings and easy-cleaving oxide coatings, thermodynamic stability and phase compatibility at high temperature are of major concern in the usefulness of the resultant composite.[2,8]

Reaction-formed or *in situ* toughened oxide composites, such as oxide–oxide eutectics, may be able to circumvent the chemical compatibility problems, but must still be engineered to increase the fracture toughness. Oxide–oxide eutectics have demonstrated thermody-

TABLE I. Starting melt compositions.

Starting composition (wt%)	Target interphase
80.0% YAE 1.7% CaO 18.3% WO_3	$CaWO_4$
85.0% YAE 3.0% CeO_2 12.0% Al_2O_3	$CeAl_{11}O_{18}$
56% YAE 20% CaO 24% Al_2O_3	$CaAl_{12}O_{19}$
86% YAE 3.0% Pr_2O_3 11% Al_2O_3	$PrAl_2O_6$
86% YAE 3.0% Nd_2O_3 11% Al_2O_3	$NdAl_2O_6$
86% YAE 8.0% La_2O_3 6.0% Nb_2O_5	$LaNbO_4$
85% YAE 3.0% La_2O_3 12% Al_2O_3	$LaAl_2O_6$
86% YAE 6.0% La_2O_3 8.0% Ta_2O_5	$LaTaO_4$
86% YAE 6.0% Y_2O_3 8.0% Nb_2O_5	$YNbO_4$
87% YAE 5.0% Y_2O_3 8.0% Ta_2O_5	$YTaO_4$

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namic stability and phase compatibility to temperatures beyond 1700 °C.[9] For example, the directionally solidified, YAG/alumina eutectic (YAE) has shown promise in the past as a high-temperature, reaction-formed, ceramic composite.[10] YAE has shown creep resistance and high-temperature strength (1650 °C) superior to that of single-crystal sapphire.[11] YAE is chemically stable up to the eutectic point of 1826 °C in air.[12] In previous work, however, YAE has shown unacceptably low fracture toughness values.[13]

This study explores the viability of creating a weak YAG/alumina interface during eutectic formation from melt solidification. Rare-earth oxides are introduced into the melt as a means of achieving either a weak interphase at the YAG/alumina interface or a weakened YAG/alumina interface via large-ion segregation. Interface weakening via additive segregation was previously explored in YAG single-crystal/alumina powder compacts by Sambasivan *et al.*[14] The current approach requires that the weak interface should increase the room-temperature fracture toughness of the composite while maintaining the eutectic microstructure of the binary eutectic that is necessary for the desired high-temperature properties. In this research, three questions are being addressed: (i) What is the effect of a small ternary addition upon the microstructure and crystallography of the stable binary YAG/alumina eutectic?, (ii) Will oxide additives segregate to the YAG/alumina interfaces?, and (iii) Will oxide additive segregation enhance crack deflection at the interfaces?

TABLE II. Identification of primary melt phases using x-ray diffraction.

Target interphase	Phases present in XRD
$CaWO_4$	$YAG/Al_2O_3/CaWO_4$
$CeAl_{11}O_{18}$	YAG/Al_2O_3
$CaAl_{12}O_{19}$	YAG/Al_2O_3
$Pr_xAl_yO_z$	YAG/Al_2O_3
$Nd_xAl_yO_z$	YAG/Al_2O_3
$LaNbO_4$	YAG/Al_2O_3
$La_xAl_yO_z$	YAP/Al_2O_3
$LaTaO_4$	YAP/Al_2O_3
$YNbO_4$	YAP/Al_2O_3
$YTaO_4$	YAP/Al_2O_3

II. EXPERIMENTAL

In the absence of detailed phase diagrams, an exploratory series of melt-cooled YAG + alumina + rare-earth oxide additive composites were produced, as shown in Table I. The starting powders were placed into an Mo crucible and heated in a radio frequency (rf) induction furnace to 1950 °C under flowing argon. The samples were then air cooled to room temperature.

To answer the above questions about this processing approach, a number of structural techniques were used to analyze the melts. X-ray diffraction (XRD) and back-scattered electron images (BSE) were used to verify the crystalline identity of the phases present in the melt and to verify the existence of a eutectic microstructure. Scanning transmission electron microscopy (STEM) in conjunction with energy dispersive x-ray spectroscopy (EDX) was employed to address the segregation of additives to the interface on a nanometer scale. Lastly,

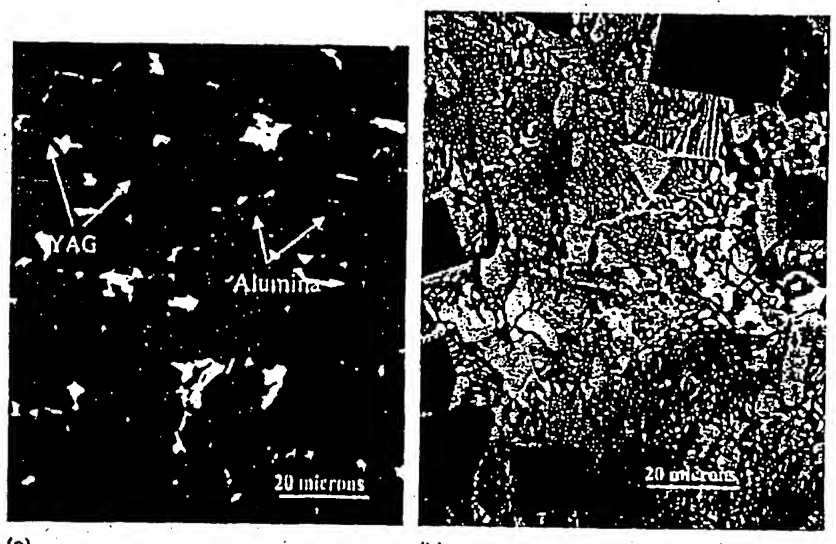


FIG. 1. (a) SEM-BSE image of "chinese script," eutectic microstructure in YAE–$CeAl_{11}O_{18}$. Bright areas indicate Ce-rich phases. (b) SEM-BSE [illegible] microstructure in YAE–YNbO. Note the large, blocklike areas of pro-eutectic alumina

micro-indentation was used to ascertain what effect interfacial segregation had on the interfacial crack behavior.

A portion of each melt-cooled sample was crushed into a powder and placed into an x-ray diffractometer to determine the crystalline phases present in the melt. Scanning electron microscope (SEM) samples were cut from the melt and petrographically prepared for microstructural characterization, using a Hitachi S-570 SEM. Transmission electron microscopy (TEM) samples were cut, petrographically thinned, and then Ar ion-milled to electron transparency. STEM-EDX microanalysis was performed using the Hitachi HF2000 c-FEG-TEM/STEM. Indentation studies were performed by making Vicker's indentations on polished samples using a diamond-tipped microindenter with 1-kg load and 10-s hold time.

III. RESULTS AND DISCUSSION

A. Microstructural analysis

Powder XRD spectra from the ten systems revealed partial success in retaining the YAG and alumina phases in six of the ten different melt compositions (Table II). The other four systems were composed primarily of yt-

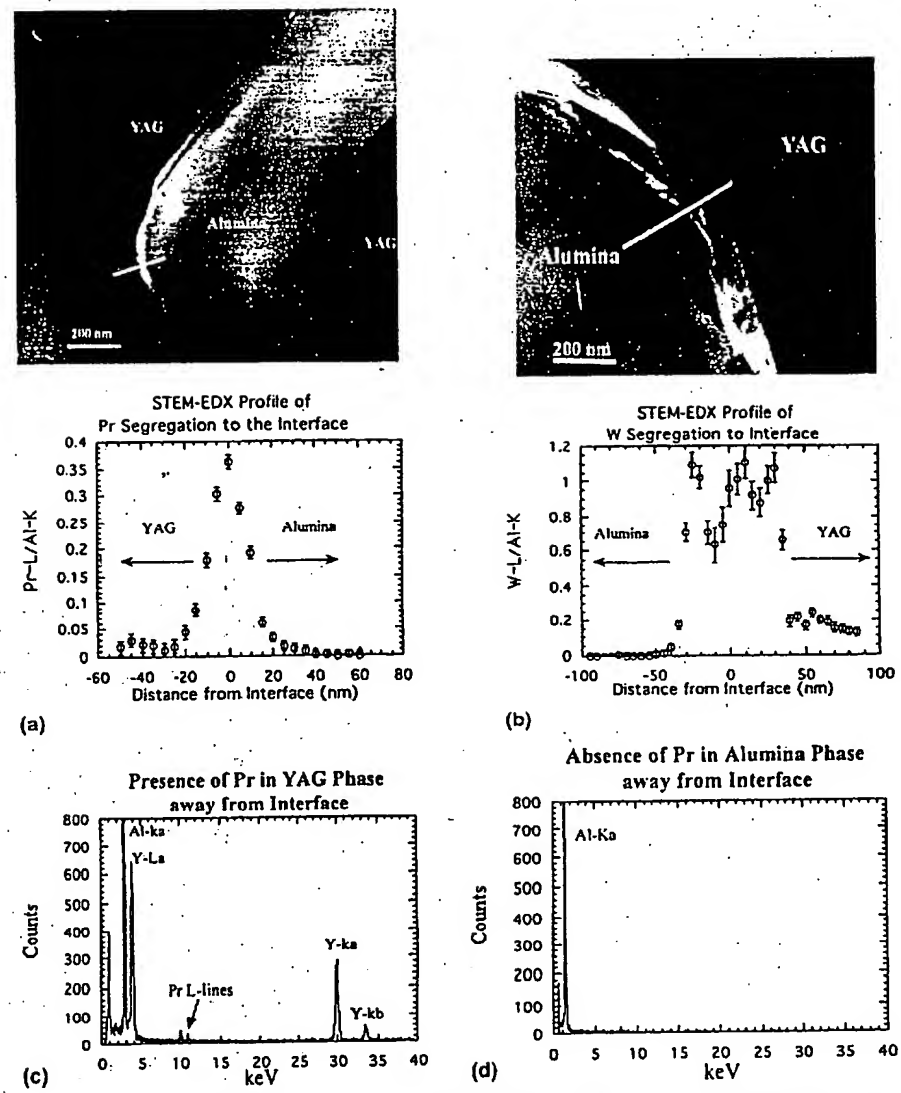


FIG. 2. (a) STEM-EDX profile across YAG/alumina interface in YAE–$Pr_xAl_yO_z$ system, indicating segregation of Pr ions to the interface. (b) STEM-EDX profile across YAG/alumina interface in YAE–$CaWO_4$ system, indicating segregation of W ions to the interface. (c) EDX spectra from YAG phase 60 nm away from the interface demonstrating a finite solubility of Pr in YAG. (d) EDX spectra from alumina phase 60 nm away from the interface showing no apparent solubility of Pr in alumina.

trium aluminum perovskite (YAP) and alumina. Of the ten systems processed as melts, only the YAE–$CaWO_4$ system showed evidence of the target interphase in the powder XRD data. It is possible, however, that target interphases exist in the other nine systems, but in quantities too small to be detected by XRD.

Back-scattered electron images from the SEM displayed a variety of microstructures for the various systems. Only the systems which showed both YAG and Al_2O_3 phases in the XRD data possessed a eutectic, "chinese script" microstructure with small regions of additive-rich oxide [Fig. 1(a)]. Additive-rich interphases were observed at some, but not all, interfaces in the eutectic microstructure. Samples with the YAP phase present possessed a much coarser, faceted microstructure [Fig. 1(b)] with large regions of a pro-eutectic phase present. The microstructure of samples also varied with location in the melt, particularly for the systems containing YAP.

The diversity of microstructures and phases within the composites demonstrates the difficulty of the *in situ* toughening approach. The observation of systems containing YAG + alumina + oxide additive in the melt gives some credence to the viability of this approach for interface control. By contrast, the dramatic departure from the eutectic microstructure and phases of the other systems demonstrates the complexity of the thermodynamics and kinetics. More *a priori* thermodynamic information about these systems would greatly aid the fabrication of these *in situ* composites. To date, however, only two of the ten systems (Y_2O_3–Al_2O_3–Nd_2O_3[15] and Y_2O_3–Al_2O_3–CaO[16]) have at least partial phase diagrams published.

B. Interfacial segregation

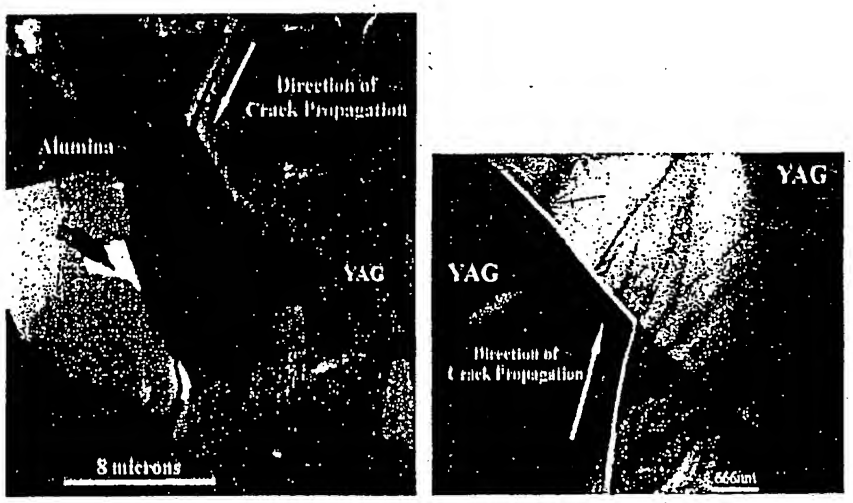
STEM-EDX analysis showed increased levels of rare-earth ions at the interfaces of several systems. Figures 2(a) and 2(b) show STEM-EDX lines profiles taken for the YAE–Pr_2O_3 and YAE–$CaWO_4$ systems. Both profiles show a large relative increase in the levels of Pr and W at the interface, respectively. In addition, small amounts of Pr and W were detected well within the YAG phase, away from the interface, demonstrating a finite solubility of these large ions in YAG [Fig. 2(c)]. No solubility of these ions was detected in the alumina phase [Fig. 2(d)].

The observed segregation of rare-earth ions to the YAG/alumina interfaces can be understood in terms of the energetics of the system as a whole. The system is taken to be the YAG phase on one side, the alumina phase on the other side, and the YAG/alumina interface connecting the two. The YAG/alumina interface in YAE is reported to be an "equilibrium," low-energy structure, the energy of this interface, the segregation may substantially lower the energy of the crystals on either side from having such large ions in solution, particularly in view of the tight lattice structure of alumina. Interfacial segregation of Y and La ions has been observed in polycrystalline alumina.[18] These findings are in agreement with the observation that no Pr was detected in the alumina only 20 nm away from the interface. However, the solubility of rare-earth ions in YAG is in keeping with the extensive use of YAG/rare-earth ion (e.g., Nd, Ce, Pr) solutions for optical materials[19] and with recent surface segregation studies in YAG.[20] The formation of an additive-rich interphase along some YAG/alumina boundaries provides further evidence for the idea that the total system energy is lowered by segregation at the expense of increased interfacial energy (Fig. 3). The segregation of additive ions to the interface is necessary for the *in situ* toughening approach of composite interface design. If ions can be made to segregate to the interface from the melt, then perhaps they will be able to decrease interfacial fracture toughness. To decrease the interfacial fracture toughness, however, the segregated ions must weaken the interface and not strengthen it.

C. Indentation response

The cracks observed from Vicker's indentations showed some evidence of following the microstructural pattern demonstrated in the above discussion. No in-

FIG. 3. Formation of Pr-rich interphase along YAG/alumina inter-



(a) (b)

FIG. 4. (a) SEM image of large angle crack deflection at a YAG/alumina interface in the YAE–$Pr_xAl_yO_z$ system. (b) Bright-field TEM image of large angle crack deflection at a YAG/alumina interface in the YAE–$Pr_xAl_yO_z$ system.

creased deflection of cracks was observed in any of the samples containing YAP. Samples containing YAG and alumina displayed some deflection of cracks in both the SEM and TEM [Figs. 4(a) and 4(b)], but also displayed areas where cracks propagated seemingly unimpeded.

The deflection of cracks at interfaces may be connected with the observed segregation of ions to interfaces. In Fig. 4(b), a large angle deflection of a crack is observed at an interface which was also determined to be rich in Pr content by STEM-EDX microanalysis. The statistics on this trend, however, are not yet sufficient to make definitive claims about the potential of this approach for increased fracture toughness in directionally solidified YAE materials. Determination of the effect of interfacial segregation upon crack deflection will require further, quantitative mechanical testing in combination with microanalysis.

IV. CONCLUSIONS

In this study the validity of chemically controlling interfacial toughness in reaction-formed composites was explored. It was shown that even with limited *a priori* thermodynamic information, it was possible to create a binary eutectic + additive microstructure that retained the microstructure and crystallography of the pure, binary eutectic. In addition, rare-earth series ions were observed to both segregate to the YAG/alumina interface and in some cases to form an interphase. Some evidence of increased crack deflection at these interfaces was observed, but further mechanical studies need to be done to determine the extent of any possible composite toughening.

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